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PATENT SPECIFICATION

(11) 1 550 382

(21) Application No. 19662/76 (22) Filed 13 May 1976
(31) Convention Application No. 579181
(32) Filed 20 May 1975 in
(33) United States of America (US)
(44) Complete Specification published 15 Aug. 1979
(51) INT CL² C08F 2/46 20/18
(52) Index at acceptance
C3V BC BF
C3P DG

(19)

(54) ACRYLIC ESTER-BASED RADIATION CURABLE COMPOSITIONS

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is concerned with radiation curable compositions comprising isobornyl acrylate and photoinitiator, more particularly radiation curable coating and ink compositions, sheets and the use of isobornyl acrylate as a reactive diluent.

It is well known in the art to deposit polymerizable liquid coatings on substrates and then to dry and cure such coatings by passing them through ovens to crosslink the coatings. It is also known in the art to use coatings which are curable by exposure to actinic radiation such as ultra-violet rays or that from plasma arc radiation sources, as well as by exposure to high energy ionizing radiation such as electron beam radiation. These systems have disadvantages in that either ovens are required or that, in radiation curable coatings, oxygen inhibition of the polymerization of the coating may occur, or it may be necessary to employ solvents to decrease the viscosity of the coating for application purposes.

Due to energy and raw material shortages, increasingly strict air pollution standards and safety regulations the search is continuing for one hundred percent polymerizable systems, i.e., compositions which have no highly volatile components but which contain reactive viscosity reducing diluents which become either the sole cured film or part of the cured film. Such types of compositions are known, for example, multifunctional acrylates, methacrylates and itaconates of pentaerythritol, dipentaerythritol and polypentaerythritols and others disclosed in U.S. Pat. Nos. 3,551,235; 3,551,246; 3,551,311; 3,552,986; 3,558,387 and 3,661,614.

Two U.S. patents which disclose radiation cure of monofunctional acrylates are U.S. Pat. No. 3,783,006, which describes a wide number of acrylate monomers for use as diluents in polymer syrups which are cured on metal containers via electron beam radiation and U.S. Pat. No. 3,772,062, which also describes the use of various diluents in the curable coatings.

We have now found that isobornyl acrylate may be used in radiation curable compositions, such as coating compositions, as a reactive diluent in 100% curable systems (i.e. containing only isobornyl acrylate, photoinitiator and optionally at least one other radiation polymerisable component) and may confer on such compositions a desirable balance of properties such as volatility, shrinkage, toxicity and viscosity.

Isobornyl acrylate is a known compound. One method of preparation is disclosed in U.S. Pat. No. 3,087,962.

Low volatility acrylate monomers are available such as trimethylolpropane triacrylate, pentaerythritol triacrylate and neopentylglycol diacrylate; however, these, unlike isobornyl acrylates, cure to highly crosslinked and extremely hard, brittle films. Isobornyl acrylate yields a relatively hard polymer (T_g=94°C.) but unlike the hard multifunctional acrylates does not contribute to increased crosslink density. Higher alkyl acrylates such as lauryl acrylate, isodecyl acrylate and, marginally, 2-ethylhexyl acrylate have the desired lower volatility and viscosity but their use alone as a diluent tends to promote excessive softening. However, in combination with isobornyl acrylate one can achieve an excellent degree of latitude of hardness and flexibility and viscosity control previously unobtainable with other combinations of acrylates. The polymeriza-

tion of isobornyl acrylate is accompanied by low volume shrinkage relative to other known reactive diluents thereby aiding and minimizing losses in adhesion and flexibility commonly observed in radiation curable systems. In addition, to these improvements, isobornyl acrylate is of relatively low toxicity, compared to many other ethylenically unsaturated monomers in common use.

According to the invention there is provided radiation curable compositions comprising

(a) from 1 to 99.9%, preferably from 10 to 98%, by weight of isobornyl acrylate;
(b) from 0.1 to 25%, preferably from 1 to 15%, by weight of photoinitiator;
(c) from 0 to 80%, by weight of nonradiation polymerisable oligomer, polymer or mixture thereof and, when employed, preferably from 5 to 50% by weight;
(d) from 0 to 90% by weight of pigment and, when employed, preferably from 2 to 80% by weight;
(e) from 0 to 50% by weight of plasticizer and, when employed, preferably from 5 to 40% by weight; and
(f) optionally polymerizable other ethylenically unsaturated monomer, oligomer or polymer or mixture thereof, copolymerizable with isobornyl acrylate and when employed, preferably from 5 to 95% by weight.

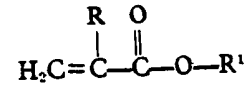
The ethylenically unsaturated monomers, oligomers and polymers optionally employed with isobornyl acrylate may be any of the known radiation polymerizable coating materials. We have found that isobornyl acrylate is compatible with material such as acrylate pendant polymers, such as acrylated epoxies, acrylated oils, acrylated urethanes, unsaturated polyesters, neopentyl glycol diacrylates; pentaerythritol triacrylate; trimethylol propane triacrylate; 1,6-hexane diol diacrylate; 2-ethylhexyl acrylate; isodecyl acrylate; hydroxyethyl acrylate; Roskydal 650 polyester (Mobay); Actomer X-70 (an acrylate functional polyester oligomer (Union Carbide)) Epocryl DRH 303.1 and the diacrylate ester of a bisphenol A epoxy resin (Shell). (Roskydal, Mobay, Actomer and Epocryl are Trade Marks).

In addition to the use of isobornyl acrylate as a reactive diluent at low to modestly high concentration in coating compositions containing reactive resins, crosslinking monomers or other monofunctional monomers, it also has considerable utility as the major if not the sole polymerizable component of a radiation curable coating composition. While very low viscosity may aid in some of these applications, e.g., for ease of surface penetration and binding to materials such as wood, leather, paper and cement, it may be desirable to add up to 80% by weight of a non-radiation reactive polymer, oligomer or mixture thereof of certain higher viscosity resins strictly for rheological control, i.e., as "thickeners". The resins do not necessarily have to be reactive in this capacity. Where the hardness of polymerized isobornyl acrylate is not required or desired, low viscosity systems of less hardness may be prepared by judicious addition of softer, low viscosity polymers. Examples of these resins include polymers of lower alkyl acrylates and methacrylates wherein the alkyl has from 1—5 carbon atoms such as methyl, ethyl, propyl, butyl and pentyl.

If desired, isobornyl acrylate can be made into soft, flexible films by the use of inert, nonvolatile plasticizers in the range of from 5 to 50% by weight. Plasticizers which can be employed include phthalate esters such as dibutyl, dioctyl, di-2-ethylhexyl, butylbenzyl diisodecyl esters, Santicizer 262 (Monsanto) and adipate esters such as dioctyl (Santicizer is a Trade Mark); phosphates such as tributoxyethyl, tributyl and tricresyl; phthalyl glycolates such as butyl phthalyl butyl glycolate; and sulfonamides such as N-ethyl-*o*-*p*-toluenesulfamide; also included are castor oil and its derivatives and polymeric types such as those disclosed in the Rohm and Haas Company booklet "Paraplex and Monoplex Plasticizers—summary of physical performance properties" published May 1968. (Paraplex and Monoplex are Trade Marks).

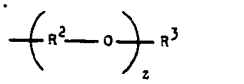
The acrylate based photocurable monomers, polymers and oligomers are generally preferred because of higher cure speed.

The ethylenically unsaturated portion of the composition other than isobornyl acrylate may comprise 0—98.9% by weight of the composition of one or more acrylate monomers or oligomers or polymers thereof; preferably at least ne monomer (or an oligomer or polymer derived from said monomer) of the formula:



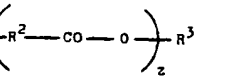
(I)

wherein R is hydrogen or methyl and R^1 is (C_1—C_{18})alkyl preferably (C_1—C_{12})alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, 2-ethylhexyl, decyl, isodecyl, dodecyl and octadecyl, aryl, for example, mononuclear aryl, such as benzyl and phenyl, cycloalkyl, for example, cycloalkyl of from 5 to 12 nuclear carbon atoms such as cyclohexyl, trimethyl cyclohexyl, cyclopentyl, cycloctyl and dicyclopentenyl, substituted aryl or substituted cycloalkyl wherein the substituent is alkyl, halo and/or hydroxy, or R^1 is



(II)

wherein R^2 is an alkylene radical of from 1 to 8 carbon atoms such as methylene, ethylene, propylene or isobutylene; z is a whole number from 2 to 25 and R^3 is as defined above for R^1, or R^1 is:



(III)

wherein R^2, R^3 and z are as described above.

Typical of the acrylic monomers which may be employed in this invention include monoacrylates, such as methyl acrylate, isopropyl acrylate, cyclopentyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, isodecyl acrylate, decyl thioacrylate, dodecyl acrylate, octadecyl acrylate, hydroxyethyl acrylate and hydroxybutyl acrylate; diacrylates, such as ethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexane diol diacrylate, polypropylene glycol diacrylate, 1,3-butane diol diacrylate and 1,4-butane diol diacrylate; triacrylates such as trimethylol propane triacrylate and pentaerythritol triacrylate or tetraacrylates such as pentaerythritol tetraacrylate.

A photoinitiator or sensitizer is added to the composition before exposing the composition to radiation. The photoinitiators or sensitizers are employed in the amounts of from 0.1 to 25% by weight of the composition and preferably from 1 to 15% by weight of the total polymerizable composition. Preferred photoinitiators employed include selected acyloins or derivatives thereof, for example, benzoin alkyl ethers such as benzoin methyl ether and benzoin ethyl ether, desyl halides such as desyl bromide and desyl chloride, desyl amine, benzophenone derivatives, acetophenone compounds, polychlorinated aromatic compounds, a combination of organic carbonyls and amines or mixtures thereof. The acetophenone photoinitiators are disclosed in U.S. Pat. No. 3,715,293. The combination of organic carbonyls and amines is disclosed in U.S. Pat. No. 3,795,807.

The invention also provides a method of coating which comprises applying a composition of the invention to a substrate and curing or drying the coating by exposure to radiation.

The compositions of this invention are dried or cured by exposure to radiation. The compositions exhibit maximum sensitivity in the range of from about 1800 to 5000 A and any source of actinic light can be employed. Suitable sources of radiation include electron beams, carbon arcs, mercury-vapor arcs, fluorescent lamps with ultraviolet light emitting phosphors, argon glow lamps, photographic flood lamps, Van der Graaf accelerators, resonant transformers, betatron linear accelerators, gamma radiation emitters and combinations thereof.

The photopolymerizable coating compositions of the present invention are useful as coatings such as adhesives, markers, vehicles for printing inks, lacquers and paints on various substrates including metals ceramic, cement, wood, plastics, textiles, paper, floor tiles, glass, roads, parking lots and airfields. The compositions are also useful in the preparation of photopolymerizable elements, i.e., a support having disposed thereon a photopolymerizable layer of a composition as described herein. Moreover, various dyestuffs, pigments, plasticizers, lubricants and other modifiers may be incorporated to obtain certain desired characteristics in the finished products.

When a photopolymerizable composition of the present invention is used as an adhesive, at least one of the lamina must be translucent when ultra-violet light is used. When the radiation source is an electron beam or gamma radiation at least one of the lamina must be capable of transmitting high energy electrons or gamma radiation respectively, and neither is necessarily translucent to light. Typical laminations include polymer coated Cellophane to polymer coated Cellophane films, treated poly-

ethylene to treated polyethylene films, Mylar polyester film to a metal substrate such as copper and the like, opaque oriented polypropylene to aluminum or polymer coated Cellophane to polypropylene. (Mylar is a Registered Trade Mark).

The photopolymerizable compositions of the present invention may be utilized for metal coatings such as in coil coating and in metal decorating. For example, in metal decorating isobornyl acrylate is useful in formulating pigmented base coats, inks and clear overprint varnishes. Glass and plastics may also be coated and the coatings are conventionally applied by dip coating, direct and reverse roller spray. Pigmented coating systems may be used for various polyester and vinyl films; polymer coated Cellophane; glass, treated and untreated polyethylene, for example, in the form of disposable cups or bottles. (Cellophane is a Registered Trade Mark). Examples of metals which may be coated include sized and unsized tin plate, tin free steel and aluminum.

The compositions may be pigmented with organic or inorganic pigments, for example, molybdate orange, titanium white, chrome yellow, phthalocyanine blue and carbon black, as well as colored with dyes. Stock which may be printed includes paper, clay coated paper and boxboard. In addition, the compositions of the present invention are suitable for the treatment of textiles, both natural and synthetic, for example, in vehicles for textile printing inks or for specialized treatments of fabrics to produce water repellency, oil and stain resistance, crease resistance and the like. A general ink formulation would be the vehicle of the composition of 1—99.8% by weight of isobornyl acrylate, 0—98.8% by weight of an ethylenically unsaturated monomer, oligomer or polymer or mixture thereof, 0.1—25% by weight of photoinitiator and 0.1—90% by weight of pigment based on the total vehicle ink composition.

Photopolymerizable elements of this invention comprise a support, for example, a sheet or plate, having superimposed thereon a layer of the above described photopolymerizable compositions. Suitable base or support materials include metals, for example, steel and aluminum plates, sheets and foils. Also films or plates composed of various film forming synthetic resins or high polymers, such as addition polymers, and, in particular, vinyl polymers, for example, vinyl chloride polymers; vinylidene chloride polymers; vinylidene chloride copolymers with either vinyl chloride, vinyl acetate or acrylonitrile; and vinyl chloride copolymers with vinyl acetate or acrylonitrile; linear condensation polymers such as polyesters, for example, polyethylene, terephthalate; and polyamides. Fillers or reinforcing agents can be present in the synthetic resin or polymer bases. In addition, highly reflective bases may be treated to absorb ultra-violet light or a light absorptive layer can be transposed between the base and photopolymerizable layer.

Photopolymerizable elements can be made by exposing to ultra-violet light selected portions of the photopolymerizable layer thereof until addition polymerization is completed to the desired depth in the exposed portions. The unexposed portions of the layer are then removed, for example, by use of solvents which dissolve the monomer or prepolymer but not the polymer.

As stated above, any suitable source of actinic energy may be used, for example a 200 watt/lineal inch, medium pressure, mercury arc source. Factors varying the rate at which a photopolymerizable composition will dry include the specific ingredients in the composition, concentration of the photoinitiators, thickness of the material, nature and intensity of the radiation source and its distance from the material, the presence or absence of oxygen and the ambient temperature.

The compositions of the present invention are generally employed as films having a thickness of from 0.1 to 30 mils, and preferably from 0.2 to 10 mils.

One embodiment of the invention provides sheets prepared from the radiation curable compositions. The sheets may have a thickness of from 30 to 1000 mils.

Some preferred embodiments of the invention will now be more particularly described in and by the following Examples, in which all parts and percentages are by weight unless otherwise stated. Example 8 is a comparative Example.

The following is a list of either how various tests were conducted or a reference to where the tests are described:

Viscosity—

Where reported in centipoise (cps.), viscosities were determined with a Brookfield Viscometer at room temperature. "Paint Testing Manual", Gardener and Sword, 12th edition, 1962, p. 178.

Where reported in centistokes, viscosities were determined with Gardner Bubble Standards. "Paint Testing Manual", Gardener and Sword, 12th edition, 1962, p. 172.

Tukon Hardness—
"Paint Testing Manual", Gardner and Sword, 12th edition, 1962, p. 135.

Pencil Hardness Test—
"Paint Testing Manual, 12th edition, Gardener and Sword, 12th edition, 1962, p. 147.

Gardner Impact Test—
"Paint Testing Manual", Gardner and Sword, 12th edition, 1962, p. 147.

Mar Resistance Test—
Mar resistance was determined by lightly scratching the coating surface with the back of a fingernail (a commonly accepted practice in the coating industry).

Cross-cut Adhesion Test—
"Paint Testing Manual", Gardner and Sword, 12th edition, 1962, p. 160.

Water Immersion Test (150°F.)—

The water immersion test at 150°F. for 30 minutes simulates pasturization of a beer can coating and measures a coatings resistance to blushing, blistering and/or loss of adhesion.

EXAMPLE 1

Composition of Isobornyl acrylate, Pentaerythritol triacrylate and 2-Ethylhexylacrylate

The four 100% polymerizable clear protective liquid coatings of the compositions disclosed in Table I (infra) are prepared by admixing the components in the order given in conventional equipment until clear and homogeneous. The coatings are then applied to aluminum test panels (Alodine 1200S) by drawdown to yield films of 1.5 mil thickness and, finally cured to a dry, tack free state by passage at 7.5 feet per minute under two 200 watt/lineal inch Hanovia medium pressure mercury arc lamps mounted in parabolic reflectors. (Hanovia is a Registered Trade Mark). The cured films are evaluated for Tukon indentation hardness, pencil hardness and impact strength. The findings evidence the improved balance of coating viscosity, film hardness and film toughness that is achieved employing isobornyl acrylate.

TABLE I

Coating Composition (parts by weight)	A (Control)	B (Control)	C	D
Pentaerythritol triacrylate (PETA)	100	25	20	15
2-Ethylhexyl acrylate (EHA)	0	75	60	45
Isobornyl acrylate (IBOA)	0	0	20	40
Benzoin ethyl ether (BEE)	3	3	3	3
System Properties				
Liquid viscosity (centipoise)	860	4	4	4
Cured Film Tukon Hardness	>30	~2	~2	~2
Pencil Hardness	4H	3B	HB	F
Direct Impact (in.-lb.)	<2	6	10	15

EXAMPLE 2

Metal Coating of Isobornyl acrylate, Pentaerythritol triacrylate and Actomer X-80

A 100% polymerizable liquid coating useful as a protective coating for metal is prepared by mixing, until clear and homogeneous, Actomer X-80 (Actomer is a Trade Mark), a high viscosity acrylate functional resin (Union Carbide) with isobornyl acrylate, pentaerythritol triacrylate (crosslinker) and benzophenone/methyl diethanolamine (photosensitizer system) in the proportions given below:

Coating Composition	Parts by Weight
Actomer X-80	40
Isobornyl acrylate	40
Pentaerythritol triacrylate	20
Benzophenone	2
Methyl diethanolamine	3

The liquid coating (viscosity—350 centistokes) was applied to aluminum test panels by a wire wound rod to yield a film thickness of 0.25 mils and then cured by the procedure described in Example 1. The cured coating (pencil hardness 2H) has excellent mar resistance, adherence and is unaffected by immersion in water at 150°F. for one hour.

EXAMPLE 3

Coating of Isobornyl acrylate and Epocryl DRH-303.1

A 100% polymerizable liquid coating is prepared by mixing until clear and homogeneous Epocryl DRH-303.1, a high viscosity diacrylate ester of a bisphenol A epoxy resin (Shell), with isobornyl acrylate and diethoxyacetophenone (photosensitizer) in the proportions given below.

Coating Composition	Parts by Weight
Epocryl DRH-303.1	45
Isobornyl acrylate	55
Diethoxyacetophenone	2

The liquid coating has a viscosity of about 350 centistokes and is applied to aluminum test panels by wire wound rod to yield a film thickness of 0.25 mils and then cured by the procedure described in Example 1. The cured coating (pencil hardness 2H) has very good mar resistance, adherence and is unaffected by immersion in water at 150°F. for 1 hour.

EXAMPLE 4

Comparison of Isobornyl acrylate with Styrene and Isobornyl methacrylate

The utility of isobornyl acrylate as a diluent monomer for 100% polymerizable unsaturated polyester coatings conventionally employing styrene diluent is afforded by the comparative cure results of Table II. Therein, the unsaturated polyester resin Roskydal 650 (Mobay) was dissolved in styrene, isobornyl acrylate, as well as in isobornyl methacrylate to demonstrate the cure speed advantage of the preferred acrylate moiety. The coatings were cast to yield 1.5 mil films on aluminum test panels and cured as described in Example 1.

TABLE II

Coating Composition (parts by weight)	A	B	C	D	E	F
Roskydal-650	0	0	0	65	65	65
Styrene	100	0	0	35	0	0
Isobornyl acrylate	0	100	0	0	35	0
Isobornyl methacrylate	0	0	100	0	0	35
Benzoinethyl ether	3	3	3	3	3	3
Cured Film Properties						
Appearance	evaporates	cures	no cure liquid	some cure heavy mar	cures mar free	some cure heavy mar
Pencil Hardness	NT*	3H	NT	NT	F	NT

* not tested

EXAMPLE 5

Composition of Isobornyl acrylate, 2-Ethylhexyl acrylate and Actomer X-80

A 100% polymerizable coating is prepared by admixing the following ingredients until clear and homogeneous. The solution has a viscosity of 340 centistokes:

Coating Composition	Parts by Weight
Actomer X-80	60
Isobornyl acrylate	20
2-Ethylhexyl acrylate	20
Methyl diethanolamine	3
Benzophenone	2

The liquid coating is filmed with a No. 40 wire wound rod on a piece of commercial vinyl asbestos type flooring tile and cured as described in Example 1 to afford a glossy, resilient, mar resistant and adherent protective finish on the tile.

EXAMPLE 6

Isobornyl acrylate with Nonradiation Reactive Polymers

The compositions of Table III are prepared by admixing the components in conventional equipment until clear and homogeneous. The wet coatings are applied with a No. 4 wire wound rod to aluminum test panels (0.25 mil film thickness) and cured as described in Example 1.

TABLE III

Coating Composition (parts by weight)	A	B	C	D
Isobornyl acrylate	100	20	20	20
Isobutyl methacrylate polymer ($\overline{M}w$ 80,000; Tg 50°C.)	0	80	0	0
Methyl methacrylate 70/Ethyl acrylate 30 copolymer-($\overline{M}w$=90,000; Tg 60°C.)	0	0	80	0
Methyl methacrylate 55/Ethyl acrylate 45 copolymer-($\overline{M}w$=70,000; Tg 35°C.)	0	0	0	80
Benzoinethyl ether	3	3	3	3
System Properties				
Liquid viscosity (centipoise)	7	240	3700	960
Cured Film Pencil Hardness	3H	H	2H	H

EXAMPLE 7

Coating of Concrete and Wood

Composition A of Example 6 is applied by wiping a thin layer on a concrete test slab and a wood test slab. The slabs were then cured by the procedure as described in Example 1 to yield water repellent, protective hard finishes on both substrates.

EXAMPLE 8

Rates of Volatilization

The volatility characteristics of isobornyl acrylate is compared with other diluent monomers. Seven (7) cm. diameter circles of Whatman No. 1 filter paper is saturated with monomer (*ca.* 1—1.3 gm.) and weight loss is monitored as a function of time, the specimens being placed in a laboratory hood of modest air velocity. (Whatman is a Registered Trade Mark). Weight loss versus time is linear through at least 80% loss of the samples. The resulting rates of weight loss, expressed in milligrams per minutes from the specified samples are given below.

Monomer	Rate of Volatilization (mg./min.)
Styrene	19
Butyl acrylate	17
Cyclohexyl acrylate	1.9
2-Ethylhexyl acrylate	0.5
Isobornyl acrylate	0.25
Isodecyl acrylate	0.1

EXAMPLE 9

Isobornyl acrylate Compositions with Plasticizers

Composition (parts by weight)	A	B	C
Isobornyl acrylate	100	95	90
Santicizer 262[1]	0	5	10
2,2-Diethoxyacetophenone	2	2	2
Cured Film Properties			
Knoop Hardness	14	10	4.4
Mandrel Flexibility (diameter passed, in.)	>6	>6	4

[1]Santicizer 262 is a monomeric phthalate type plasticizer (Monsanto) of undisclosed composition having a molecular weight of 396.5

WHAT WE CLAIM IS:—

1. A radiation curable composition comprising
(a) from 1 to 99.9% by weight of isobornyl acrylate;
(b) from 0.1 to 25% by weight of a photoinitiator;
(c) 0 to 80% by weight of nonradiation polymerizable oligomer, polymer or mixture thereof;
(d) from 0 to 90% by weight of pigment;
(e) from 0 to 50% by weight of plasticizer; and
(f) optionally radiation polymerizable other ethylenically unsaturated monomer, oligomer or polymer or mixture thereof copolymerizable with isobornyl acrylate.

2. A composition as claimed in Claim 1 comprising:
(a) from 10 to 98% by weight of isobornyl acrylate; and
(b) from 1 to 15% by weight of photoinitiator.

3. A composition as claimed in claim 1 or 2 which is in the form of a 100% radiation polymerizable composition which contains only components (a) and (b) and optionally component (f).

4. A composition as claimed in any preceding claim wherein the photoinitiator comprises an acyloin or derivative thereof; desyl halide, desyl amine, benzophenone derivative, acetophenone compound, polychlorinated compound, a combination of organic carbonyl and amine or mixture thereof.

5. A composition as claimed in any preceding claim containing from 5 to 95% by weight of radiation polymerizable other ethylenically unsaturated monomer, oligomer or polymer or mixture thereof copolymerizable with isobornyl acrylate.

6. A composition as claimed in any of Claims 1, 2 or 4 containing from 5 to 50% by weight of nonradiation polymerizable oligomer, polymer or mixture thereof.

7. A composition as claimed in any of Claims 1, 2 or 4 containing from 2 to 80% by weight of pigment.

8. A composition as claimed in any of Claims 1, 2 or 4 containing from 5 to 40% by weight of plasticizer.

9. A composition as claimed in Claim 1 substantially as described in any of the foregoing Examples 1—7 and 9.

10. A method of coating which comprises applying a composition according to any of Claims 1 to 9 to a substrate and curing or drying the coating by exposure to radiation.

11. A method as claimed in Claim 10 wherein the coating is dried or cured by electron beam.

12. A method as claimed in Claim 10 wherein the coating is dried or cured by actinic light.

13. A substrate having thereon a radiation cured composition according to any of Claims 1—9.

14. A substrate as claimed in Claim 13 wherein the cured composition is from 0.1 to 30 mils thick.

15. A substrate as claimed in Claim 13 wherein the cured composition is from 0.2 to 10 mils thick.

16. A sheet prepared from a radiation cured composition according to any of Claims 1—9.

17. A sheet as claimed in Claim 16 having a thickness of 30 to 1000 mils.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.